A STUDY OF THE CHEMICAL EFFECTS OF SLOW NEUTRON
IRRADIATION OF PHOSPHORUS TRICHLORIDE

by

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INTRODUCTION

The Szilard-Chalmers (40) type nuclear reaction is one of the more interesting phenomena in radiochemistry. This is evidenced by the number of publications on that subject in the last few years. Since the chemical species produced by neutron irradiation are dependent upon the bond energies of the compounds and the systems being irradiated, the effects are varied from compound to compound and system to system. Therefore a study of these effects on many compounds and systems is desirable so that the results can be predicted for related compounds. This research was undertaken on a compound not previously studied to contribute more information concerning the fundamental nature of the Szilard-Chalmers type reaction and to illuminate a little more clearly the applications of the special theory (30) put forth concerning the kinetics of this type of reaction.

It can be shown, as follows, (25) that the energy of the recoiling atom, after emitting one or more stabilizing gamma rays, is more than sufficient to break a chemical bond. The only energy available for this reaction is the energy that binds the neutron to the nucleus. Consider an atom of mass M emitting a γ-ray. Then the energy of the γ-ray $= E = mc^2 = mc \cdot c = pc$, since $p = $ momentum $= mc$. Rearranging: $P = \dfrac{E_\gamma}{c}$. Now the recoiling nucleus possesses an equal and opposite mementum, in accordance with the law of the conservation of momentum. The atom of mass M has a recoil energy

of E. Accordingly:

$$E = \tfrac{1}{2} Mv^2 \; ; \quad momentum = p = Mv; \; \therefore \; p^2 = M^2v^2.$$

$$E = \tfrac{1}{2} Mv^2 \cdot \frac{M}{M} = \tfrac{1}{2} \frac{M^2v^2}{M} = \frac{p^2}{2M}$$

Since the two momentums are equal or $P_\gamma = P$, we can substitute the momentum of the γ-ray for the momentum of the atom.

$$E = \frac{p^2}{2M} = \frac{\left(\dfrac{E_\gamma}{c}\right)^2}{2M} = \frac{E_\gamma^2}{2Mc^2}$$

1 mass unit = $(M_H c^2)$ = 931 million electron volts (mev).

Substituting:

$$E = \frac{E_\gamma^2}{1862M} \; mev \cdot 10^6 \; ev \; / \; mev = 536 \frac{E_\gamma^2}{M} \; ev.$$

Since the energy associated with a chemical bond is in the neighborhood of a few electron volts, it can be seen immediately that there is more than sufficient energy arising from this recoil process to break a chemical bond.

There are also examples in the literature (19, 26, 32) where bonds have been broken by the recoil momentum of atoms after having emitted particles, especially protons. Therefore, the Szilard-Chalmers type reaction could occur due to this particle emission.

The choice of material studied, phosphorus trichloride, arose when a source of P^{32} labelled PCl_3 was needed as a starting point in the synthesis of the insecticide parathion, (O-O-diethyl O-p-nitrophenylthiophosphate). To obtain such a phosphorus labelled phosphorus trichloride it was decided to bombard inactive PCl_3 with slow neutrons in an incomplete

Szilard-Chalmers reaction (3). After the synthesis of para-
thion was completed, (21) it was noted that the parathion was
doubly labelled, - labelled both with P^{32} and S^{35}. This
meant that sometime in the course of the bombardment, S^{35} was
synthesized in a form in which it could be taken up in the
first reaction of the parathion synthesis, which is:

$$PCl_3 + S \xrightarrow[75^oc]{AlCl_3} PSCl_3$$
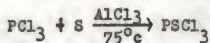
For S^{35} to be incorporated into the thiophosphoryl chloride
it had to be either in the elemental form or as already
synthesized PS^*Cl_3. Note this could be $P^*S^*Cl_3$ or PS^*Cl_3.
Further, the percentage yields on the reactions of the syn-
thesis and the amount of P^{32} incorporated into $PSCl_3$ indi-
cated a high percentage recombination of the active phos-
phorus with three chlorines apiece giving again the start-
ing molecule PCl_3. This was not entirely expected, although
it had been hoped for and so it was decided to investigate
this reaction and the Szilard-Chalmers effect upon it to
determine specifically the per cent recombination, other
chemical forms containing radioactive phosphorus, and the
chemical forms of radioactive sulfur present.

From the activities produced, the nuclear reactions
involved were as follows:
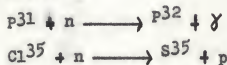
$$P^{31} + n \longrightarrow P^{32} + \gamma$$
$$Cl^{35} + n \longrightarrow S^{35} + p$$

The thermal neutron cross section for the reactions

$P^{31}(n,\gamma)P^{32}$ and $Cl^{35}(n,p)S^{35}$ are 0.2 barns (39) and 0.13 barns (19) respectively. Subsequent investigation showed that no active Cl^{36} or Cl^{38} from the reactions $Cl^{35}(n,\gamma)Cl^{36}$ and $Cl^{37}(n,\gamma)Cl^{38}$ were present as would be expected from their half-life values. As will be pointed out later, a variation in irradiation time produced a different ratio of the number of P^{32} atoms (half-life = 14.3 days (6)) to the number of S^{35} atoms (half-life = 87.1 days (22)) formed.

The Szilard-Chalmers effect (40) as first noted by these two men, consisted of the formation of water soluble active iodine after the thermal neutron bombardment of ethyl iodide. The irradiated organic liquid was shaken with water containing a small amount of iodide carrier and sodium sulfite. A considerable fraction of the active iodine (25 - min.I^{128}) was found in the aqueous layer while essentially all the unchanged target iodine atoms remained as ethyl iodide. Most of the active iodine emerged in the aqueous layer as the iodide ion. "That portion of the iodine activity which remains in the organic form is said to be 'retained' although [recombined] would be a better term, since it is quite certain that the nuclear reaction induces bond rupture in almost every instance." (44) The Szilard-Chalmers effect is, then, the breaking of chemical bonds due to thermal neutron bombardment.

The success of a Szilard-Chalmers type reaction is dependent upon the physical state or phase (14) of the material

as well as the following (16): 1) Sufficient recoil energy must be available to the nucleus on capture of the neutron so that the chemical bond can be ruptured. 2) There must be no exchange of activated atoms with inactive atoms. 3) The radioactive atoms must be chemically separable from the inactive atoms of the same element. 4) Recombination must not occur during bombardment.

In passing, it is interesting to note that this type of reaction was first used to obtain material with very high specific activity, and is, for this reason, of considerable value. With the several neutron piles now in operation the practice has come about of taking advantage of what is known as an incomplete Szilard-Chalmers process whereby the recombination to the original molecule is of more interest (3,20). This procedure has been used with considerable success to obtain labelled compounds that are difficult to synthesize. The irradiation of PCl_3 would really fall into this category, although the kinetic theory of either category is the same.

LITERATURE SURVEY

Other Szilard-Chalmers Type Reactions.

Following the work of Szilard and Chalmers in 1934 on
the reaction which bears their name, Fay and Paneth (12)
bombarded arsine (AsH_3) in the gaseous phase and ethyl io-
dide in the liquid phase with slow neutrons. Their primary
aim was to isolate active $_{33}As^{76}$ and active $_{53}I^{128}$. This
was done by the application of an electric field. It was
reported that the charge acquired by the active atoms had
nothing to do with the mechanism of the capture of the neu-
trons, but was due to secondary processes. It was found,
also, that it was possible to increase the specific activi-
ty of active iodide ion by utilizing this method when methyl
and butyl iodides were bombarded, and the concentration of
active bromide ion when ethyl, butyl, methylene, and ethy-
lene bromides were used.

In 1936, Glückauf and Fay (20) synthesized quite a
number of the simpler labelled organic molecules such as
methyl bromide, phenyl bromide and ethyl dibromide by slow
neutron bombardment of the mother molecule or an homologous
compound quite similar in structure. These were the first
compounds synthesized by use of the incomplete Szilard-
Chalmers type of reaction - the type of reaction utilized in
this current investigation.

High specific activity phosphorus was first isolated in
1937 by Erbacher and Philipp (11). They used the (n,Γ) re-

action on triphenyl phosphate. The work by Libby (29) in 1940 and subsequent work by him and his coworkers laid the foundation for his present theory of the kinetics of this Szilard-Chalmers type reaction. Data were given for the per cent of the radioactivity recovered (called retention) on a variety of organic and inorganic compounds under various conditions of acidity, basicity, physical states, and buffer states. Some of the more interesting data deal with retention of tri- and quinquevalent phosphorus on bombardment of phosphorus acids and their sodium salts. The retention of activity was near 50% under all the various conditions. These data further substantiated the rough rule that the results of the recoils would correspond to the distribution of the bonding electrons among the products about as they were distributed in the bonds broken, and the observation that the organic halides had high retentions in the pure state owing to the collisions between the recoiling X^* particles and the halide molecules transferring the energy to nonradioactive atoms (generally halogens) and leaving the residual free radical or ion in the same reaction "cage" with the stopped X^* particle.

Aten (1) bombarded $Na_2SO_4 \cdot 10H_2O$ and $Na_2SO_3 \cdot 7H_2O$ in 1942, in an $S^{32}(n,p)P^{32}$ nuclear reaction. The phosphate and phosphite fractions were isolated with the following results: In the sulfate 91% of the P^{32} occurred as phosphate and 9% as phosphite (or other phosphorus compounds of lower

valencies). In the sulfite 40% of the P^{32} was found in the phosphate and 60% in the phosphite fraction indicating that the crystal lattice influenced the fate of the phosphorus ion to a great extent.

In an article published in 1942 and again in two published in 1943, Daudel (7,8,9,) submitted the theory of negatron emission and some of the experimental data that led to that theory. It was said that the Szilard-Chalmers effect was due to negatron emission but the investigations were on inorganic salts only. Gibert, Roggen, and Rossel (19) bombarded chlorine samples with slow neutrons and reported in 1944 that the only reaction identified was Cl^{35} (n,p)S^{35} having a reaction energy of 0.52 $\pm$ 0.04 mev. and an effective cross section of 1/4 that of the reaction N^{14} (n,p)C^{14}.

Libby (30), in 1947, reviewed the variety and nature of the recoil excitations suffered by atoms whose nuclei partake in the various possible nuclear reactions, and developed further the kinetics of the Szilard-Chalmers type reaction. It was stated that the chemical kinetics of the recoiling (frequently radioactive) atoms was treated by considering first the nature of the cooling deceleration process (predominantly non-ionizing collisions), and second, subdividing the problem into one class involving no change in atomic number, i.e. the Szilard-Chalmers reactions and another class in which changes in atomic number occurred. The essential features of the mechanism for the first class

established that the classical collision theory and the
Franck-Rabinowitsch "cage" (15) were sufficient to explain
the main facts. Ionic solids were the principal constitu-
ents in the second class but few data were available.

In 1949, Koski (26), published a paper in which he came
to some conclusions that could bear considerable importance
to this paper. It was found that when thermal neutron-
irradiated solid KCl was dissolved in water containing sul-
fite, sulfate, and sulfide ion carriers all the S^{35} appeared
in the sulfate fraction. If the KCl was heated and out-
gassed prior to the irradiation, it was found that as much
as 85% of the activity was in the sulfide fraction. There
was essentially no activity in the sulfite fraction if
sulfide carrier was present, a good indication that the
S^{35} was not present in the KCl crystals as SCl_2 or S_2Cl_2
or other compounds that hydrolyse to sulfite ion such as
thionates and polythionates. If sulfide ion was absent,
the activity normally found in the sulfide fraction was
found in the sulfite fraction; if both sulfide and sulfite
carriers were absent, all activity was found in the sulfate
fraction.

From these data, Koski concluded that the S^{35} formed
in an oxygen-free KCl crystal was in the form of $S^=$ or S,
and the two were indistinguishable because of rapid iso-
topic exchange. In the absence of sulfide carrier in the
water, the reduced S^{35} was oxidized by dissolved oxygen to
sulfite, or to sulfate if both sulfide and sulfite carriers

were absent. This oxidation of "carrier free" $(S^{35})^=$ or S^{35} to sulfate (oxidation was complete in less than three minutes at room temperature in the presence of solid KCl) was very much more rapid than the oxidation of macro amounts of $S^=$ or S. In the absence of dissolved oxygen, it was found that aqueous solutions of "carrier-free" $(S^{35})^=$ or S^{35} were quite stable.

Koski reasoned that the irradiated chlorine was an ion in the crystal lattice, and the proton on leaving the compound nucleus would reduce the nuclear charge by +1 leaving the residual sulfur fragment with a double negative charge. This charge could have been reduced by electron capture by the proton as it moved through the electronic field of the sulfur fragment. Such considerations would lead one to believe that the sulfur activity should be present as sulfide ion or possibly elementary sulfur.

In 1949 Friedman and Libby (17) published a comprehensive study of the bombardment of propyl bromide and isopropyl bromide and the application of those data to the extension of Libby's theoretical considerations. It was reported that the principal part of the radio-bromine that resisted aqueous extraction (organically combined) was propyl bromide. The ratio of the propyl to the isopropyl bromide formed by the irradiation of either compound was 2.5. The irradiation of propyl bromide cooled to liquid-nitrogen temperatures, produced the same relative yield

of both compounds. However, at the lower temperature, the yield of the dibromides was much larger, the yield increasing by a factor of four. These results were interpreted as evidence that the bromine substitution was a reaction occurring largely in the high-energy range where the chemical bonds involved were negligible, and that the hydrogen substitution occurred in the lower-energy range where the recoiling bromine atoms collided with the molecule as a whole in an inelastic manner rather than with a single atom as was postulated in the high-energy range. The difference in temperature dependence of the two types of substitution reactions would appear to be due to the difference in magnitude of the energies involved. The fact that the irradiation of isopropyl bromide produced 2.5 times as much propyl as isopropyl was taken as further evidence of the extremely energetic nature of the bromine substitution reaction. The free radical apparently had sufficient energy to be isomerized before recombination occurred in the solvent "cage".

Rieder (36) in 1950, published a study of the variation of retention of radioactive manganese in permanganate with the change in concentration and hydroxyl ion concentration. In 1950 Rieder, Broda, and Erber (37) also published another paper on the fragments that resulted from the bombardment of permanganate ion and the dependence of the relative concentration of Mn^*O_2 and $Mn^*O_4^-$ on pH, concentration, temperature, and the presence of foreign ions.

In 1951, Müller and Broda (33) published a study of
the Szilard-Chalmers effect on the oxygen acids of arsenic
in both solid and dissolved states. Here the pH, concen-
tration, and temperature effect retention only slightly.
In solution the distribution of activity is As(III) 85%
and As(V) 15% regardless of the original oxidation state.
In solid arsenites and arsenates the distribution favored
As(V).

In June 1951, Jordan (24) observed that manganese as
permanganate subjected to the Szilard effect exhibited
valence changes from VII to II first and then eventually
into Mn(IV).

Also in 1951, Major and Süe (31) reported on the effi-
ciency of the separation of radioactive chlorine from solid
hexachloroethane and carbon tetrachloride by the Szilard-
Chalmers effect with the following conclusions. The con-
clusions were: 1) Efficiency was greater in the liquid than
in the solid state. 2) Within a rather large experimental
error, efficiency was independent of concentration. 3) Ef-
ficiency decreased exponentially with duration of irradiation.
This was explained as due to the decomposition of inactive
molecules by γ-rays and neutrons, and the recombination of
active atoms.

In a publication by McCallum and Holmes (32) in 1951
the belief was expressed that in the bombardment of $NaClO_3$
in the solid state, with γ-rays up to 24 mev., the nuclear
reaction being $Cl^{35}(\gamma,n)Cl^{34}$, the retention of the activi-

ty in the $NaClO_3$ was caused by a re-entry of the chlorine
ion rather than a failure to rupture the bond. It was
said that the recoil energy here for the Cl^{34} nucleus was
370,000 e.v.

Boyd, Cobble, and Wexler (4) noted in 1952 that the
increase of radioactive bromine retention with time in
bombarded organic halides suggested the occurrence of a
radiation recombination.

There have been two recent 1952 publications on the
Szilard-Chalmers process on solid phosphorus salts. The
first by Aten, van derStraaten, and Riesebos (2) was a
study of the irradiation of phosphorus salts such as
$Na_4P_2O_2 \cdot 10 \cdot H_2O$ and Na_2HPO_4. It was concluded that ortho-
and pyrophosphates and phosphites were all formed in the
bombardment. However, the formation of pyrophosphate was of
especial interest since secondary reactions (thermal exchange
or formation in aqueous solution during carrier extraction)
did not account for this polyatomic, electron-pair bonded
ion. It was inferred that this ion was formed by interac-
tion of the P^{32} nuclei, having high kinetic energy, with
the compound being irradiated.

The second of these papers was by Fiskell, DeLong and
Oliver (13). Phosphorus salts of calcium were bombarded
with slow neutrons and the different forms of active phos-
phorus were investigated. The major conclusions drawn from
these experiments were a) when calcium phosphates are sub-

jected to neutron bombardment in the solid state there was
considerable retention of the original chemical form; b) that
a major fraction of the remainder of the P^{32} produced appeared
in solution as hypophosphate, and c) the greatest care should
be taken to insure that the carrier P^{31} and P^{32} are present in
the same chemical form.

In another attempt to extend earlier data, Fox and
Libby (14) published a study of the hot-atom chemistry of
the propyl bromides including the effect of phase and recoil
energy on the retentions. The yields were determined for
the various organic labelled bromides formed by neutron
irradiation of liquid and solid isopropyl and propyl bro-
mides at various temperatures. The bombardment of the or-
ganic halide at the melting point (solid phase) resulted
in a threefold or larger increase in yield of certain pro-
ducts, presumably those formed by epithermal (just above
thermal) bromine atoms, and a smaller increase for the re-
mainder of the products, such as the mother molecule, pre-
sumably formed by hot reactions. Reactions occurring in
the high recoil energy range where the comparative energy
of chemical bonds were small were called "hot" and those
occurring in the range where the recoil energy was still
somewhat larger than the energy of the chemical bond, but
not over two- or three-fold larger, were called epithermal.

In the "hot" range the only collisions that led to
retention of radioactivity in the organic phase were sup-
posed to involve transfer of the momentum of the hot Br^*
atom. Thus the free radicals generated in the collision and

the stopped Br* atom were left in the same solvent cage. Therefore, reactions to form organic radiobromides were very probable. In the case of the propyl bromides it was clear that the only atom heavy enough to decelerate a Br^{82} atom in a single collision would be another bromine atom, so the original molecule was expected to be a principal product of the hot reactions.

The epithermal reactions were supposed to be influenced by solvent cage action with one important difference. The stopping of the recoiling Br* atom no longer required a collision with an inactive bromine atom since the energy and momentum of recoil could be transferred to the whole molecule by inelastic processes. The free radicals generated by the disruption of the molecule struck could be of any type, and it was expected that the formation of new molecules, different from the target molecule, was extremely likely. In other words, epithermal reactions should have led to hydrogen substitution, carbon-carbon bond rupture and replacement, and other types of fundamental chemical change, whereas hot reactions should have, in general, reformed the mother or target molecule.

If the theory outlined were correct, or essentially so, a considerable difference should have been expected by so fundamental a change in the characteristics of the solvent cage as brought about by solidification. In a general way the processes involving the most energy, the

hot reactions, should have been least affected since the solid probably would have been melted for a considerable region around the reaction site by the energy passed on to the struck Br atom as well as by that dissipated by the radioactive Br^* atom before the head-on Br collision which lead to retention (Fig.1). Therefore, relatively little difference between the liquid and solid phases might have been expected for hot reactions. The epithermal reactions, however, should have shown a much larger response to solid-ification because they occurred at the very end of the range of the recoiling atom. The epithermal reaction site, having been at the end of the range was on the surface of the mol-ten drop formed instantaneously in the solid by the recoil-ing atom. Since the epithermal site was on the surface it would have had a large fraction of its cage wall solidified by the phase change and thus rendered much less permeable (35) with a resultant large increase in probability of epi-thermal reactions. The hot sites within the drop were not subject to this effect. In either case the temperature of the phase should have had relatively less effect since even the epithermal reaction energies made thermal energies appear small in comparison. This was the explanation for the epi-thermal production of bromides of considerably higher boil-point than the mother molecule. Apparently the retentions in the solid phase depended on the energy of the recoil bromine. Thirty-six hour Br^{82} showed 93% retention in solid
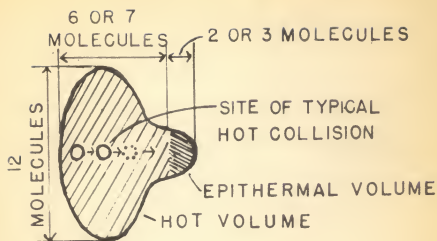
Fig. 1

Picture of a reaction volume or cage showing
sites of hot and epithermal reactions (14).

n-propyl and 80% for the 18-min. and 4.4-hr. Br^{80}. In the
liquid, no difference in retention had been observed. On
this basis it had been concluded that the average recoil
energy of the 36-hr. Br^{82} was less than those of the two
Br^{80} isomers and that the latter two differed relatively
little.

Exchange Reactions

In 1939 Voge (41) reported on exchange reactions in-
volving radioactive sulfur. In polysulfide ion the sulfur
atoms had been found to exchange places rapidly, whereas
sulfate ion was found to exhibit no exchange in 36 hours
at $100^{\circ}C$. One of the sulfur atoms in the thiosulfate ion
was rapidly transferred to a sulfite ion at $100^{\circ}C$, but the
exchange between thiosulfate and sulfide at $100^{\circ}C$ was much
slower. Sulfur dioxide and sulfur trioxide did not exchange
at temperatures appreciably below those at which dissocia-
tion of the trioxide might be expected. This was found to
be true also in the presence of platinum or water.

Sidgwick (38) reported that the exchange of radio-
active sulfur with the monochloride was very slow in the
cold, but measurable at $100^{\circ}C$.

Wilson (45) in 1938, and Hull (23) in 1941 published
information on the lack of an exchange reaction occurring
between elemental phosphorus and ortho-, pyro-, and meta-
phosphoric acids. This exchange reaction was checked in

dilute aqueous solutions, both acid and alkaline, at tem-
peratures ranging from 20°C to 100°C. Both reported that
no such exchange took place within experimental error.

In 1942 Koskoski and Fowler (27) reported on exchanges
between radiobromine and PBr_3, between radiochlorine and
PCl_3, and between radiochlorine and PCl_5 in carbon tetra-
chloride solution. All of the exchanges studied were found
to be rapid and complete in less than 3 minutes and the con-
clusion was drawn that the five halogens in PCl_5 and in PBr_5
are probably equally reactive.

Modes of Attack

Most of the experimental investigations on the effects
of the Szilard-Chalmers reaction have been either analytical
methods, with the addition of inactive carriers and hold-
back carriers, or fractional distillation methods also with
the addition of both inactive carriers and holdback carriers.
Both of these procedures were employed in this research.
However, it seemed that paper chromatography combined with
radioautography would lend itself very nicely to this pro-
blem. The idea was to chromatograph the irradiated solu-
tions of PCl_3 and then make radioautographs of them. The
R_f values would be taken from the autograph rather than
from the filter paper strip. This, then, caused an addi-
tional partial literature survey on the general field of
chromatography. Eluting agents became the primary interest

as the form and procedure were developed with available
apparatus.

In 1949 Lederer (28) published a paper on the separa-
tion of inorganic ions. The eluting agent used by him was
in a ratio of 2:1:2. He listed the R_f value for phosphate
ion as 0.04 and the R_f value for sulfate ion as 0.07.

In 1951 Müller and Wise (34) published a paper des-
cribing a scanning technique of chromatograms. Active sol-
utions were chromatographed and then passed at a regulated
speed over a very fine slit system under which a G.M. tube
was connected to a scaling circuit. Chromatograms could
be analysed in much less time than the time required for
making radioautographs. In 1951 Frierson and Jones (18)
published a similar article containing much the same mat-
erial as Müller and Wise's publication.

In a 1951 publication by Westman and Scott (43) it
was reported that 60% of a sample containing phosphates
and tetraphosphates was separated into various components
by using propanol-1, water, and 0.88 specific gravity ammon-
ium hydroxide in a ratio by volume of 60:20:20 respectively.

Ebel and Volmar (10) contributed more valuable infor-
mation in their article of 1951 which involved an inves-
tigation of the separation of ortho-, pyro-, tripoly-,
and tetrametaphosphates. The following method of pretreat-
ing the filter paper before introduction of the sample was
developed. The use of Whatman #1 filter paper did not per-
mit a convenient migration of the phosphate ion unless it

had been given pretreatment. The filter paper was washed
in dilute hydrochloric acid when a basic solvent was used
and washed in alcoholic 8-hydroxy quinoline when an acid
solvent was used. Many solvent systems were listed but
the only one utilized was the one that gave the greatest
separation of ions. This solvent system was comprised of
70% propanol-2, 30% water and 5% trichloroacetic acid.
This gave an R_f value for orthophosphate ions of 0.76.

In 1952 Bonnin and Süe (5) contributed another sol-
vent system which separated phosphates, phosphites, and
hypophosphites. The solvent contained equal volumes of
butanol-1, dioxane, and N ammonia.

EXPERIMENTAL

General

The problem at hand was the separation, identification, and semi-quantitative estimation of the radioactive products formed from the thermal neutron irradiation of phosphorus trichloride. The primary interest lay in obtaining the amount of retention of radioactive phosphorus (P^{32}) by the mother molecule and the identification of the chemical form of radioactive sulfur (S^{35}) also formed in the irradiation. Along with the desired chemical knowledge, methods and techniques of attack suitable for working with as reactive a chemical as PCl_3 had to be developed.

A radiometric method and a fractionation using inactive carriers were the two principal methods of attack. These methods have been used by other investigators also. Valuable information was obtained by the use of paper chromatography and solvent extraction from an inert media was attempted.

The radioactive material consisted originally of redistilled PCl_3. This was supplied and irradiated for one-week and three-week periods in sealed quartz vials by the Oak Ridge National Laboratory at Oak Ridge, Tennessee. These samples were shipped air express to Kansas State College, and involved a time interim of one to three days. All reactions and distillations were conducted in all-glass apparatus and due precautions taken to exclude moisture

from the system at all times. The entire research project was conducted upon a semi-micro and micro basis. All reagents used were reagent grade.

All counting data were taken with a thin-window tube and one of three scalers, 1) Berkeley Scientific Company Decimal Scaler, Model 2000, 2) Nuclear Instrument and Chemical Corporation Decimal Scaler, Model 166, or 3) Nuclear Scaler, Model 162. The thin-window tube was the usual self-quenching Geiger-Mueller type with a window thickness equivalent to 1.9 mg/cm^2 of aluminum. An Al absorber of 34.5 mg/cm^2 was inserted between the sample and the G-M tube to distinguish between phosphorus radiation (E max = 1.71 mev)(39) and sulfur radiation (E max = 0.170 mev.)(25) since the S^{35} beta particle cannot pass through this absorber.

The counting data were obtained after a small portion of the irradiated PCl_3 (25 μl to 100 μl) was added to 2 ml. of HNO_3, 1 ml. of H_2O and 0.1 gm. of $NaNO_3$ in a 10 ml. volumetric flask. The samples were oxidized, evaporated to dryness, and then diluted to the 10 ml. mark. In this way, all volatile compounds were converted to their stable non-volatile sodium salts and therefore no activity was lost in either evaporation step. From 5 μl to 100 μl samples were taken from these diluted samples, mounted on copper discs and evaporated to dryness. Counting data were obtained by counting the samples on these copper discs. All samples for

counting data were treated in this fashion.

Since S^{35} emits a low energy β^- particle, it was quite important to establish the variation in counting data, if any, arising from this mounting technique due to self-absorption of the S^{35} radiation by the sample. A series of samples from the irradiated liquid were treated in the above fashion and counted to determine this variation from sample to sample. The data are given in Table 1.

Table 1. Self absorption data.

Sample	Absorber (mg./cm² of Al)	Counts/min.	Corrected c/m
1	0	2820	2795
1	34.5	1703	1678
2	0	2665	2640
2	34.5	1581	1556
3	0	2670	2645
3	34.5	1574	1549
4	0	2800	2775
4	34.5	1600	1575
5	0	2774	2749
5	34.5	1692	1667

There is a variation from sample to sample but this variation falls within experimental error and is considered insignificant.

In order to correct the phosphorus counting rate back to zero added absorber it was necessary to know the ratio of the counting rates at zero added absorber and 34.5 mg/cm^2 of Al added absorber for P^{32} radiation. A high specific activity sample of P^{32} as phosphate was obtained from Oak Ridge and the counting rates of this, using the described mounting technique, were taken. Two separate samples gave a ratio of 1.19.

Proof of Radioactive Purity

<u>Beta Ray Energy Determination.</u> To prove that the only two radioactive elements produced in the bombardment were P^{32} and S^{35}, absorption data were taken. The data were taken on a high-boiling fraction of the irradiated sample, which arose from the addition of inactive PCl$_3$ (b.p. 74 $^{\circ}$C), PSCl$_3$ (b.p. 125°C) and S$_2$Cl$_2$ (b.p. 138°C) as carriers. A pure distilled sample of S$_2$Cl$_2$ was chosen since it contained considerable S^{35} activity as well as a comparatively energetic radiation which was proven to be P^{32} radiation as a result of this experiment. The possibility existed that both short-lived Cl^{38} and long-lived Cl^{36} had been formed in the bombardment but as these data indicated, this was not so.

The energy of the radiation from Cl^{36} would have fallen between that of S^{35} and P^{32} and the absorption curve showed that there was no extraneous radiation present. (Table 2 and

Plate I) The energy values obtained by this method for S35
and P32 radiation compared quite favorably with the accepted
literature values.

Table 2. Absorption data.

Absorber (mg. of Al/cm2)	Counts/total time	Corrected* c/m
0 +	39609/2 min.	21,000
6.10	11574/2 min.	5756
13.9	2149/2 min.	1044
21.8	2466/4 min.	586
24.1	2309/4 min.	546
27.7	2224/4 min.	525
34.5	2060/4 min.	484
39.7	2597/5 min.	488
46.6	2525/5 min.	474
54.1	3428/7 min.	449
66.6	2244/5 min.	418
89.5	1998/5 min.	369
114	2062/5 min.	356
172	2126/9 min.	205
214	1809/10 min.	150
279	1145/10 min.	84
354	674/10 min.	36
430	488/10 min.	18
558	283/10 min.	0

* Corrected counts/min. are the counting rates corrected
for background and dead time of the scaler.
+ Actually this is equivalent to 5.1 mg/cm2 of Al absorber
due to air and window thickness absorption. To correlate the
absorber values, as listed, to the absorber values on the graph
add 5.1 to each listed value.

EXPLANATION OF PLATE I

Absorption Curve for P^{32} and S^{35} Radiation
in a Composite Sample

An absorber of 34.5 mg/cm^2 of aluminum was used to
distinguish between the two activities. The almost verti-
cal portion of the curve is due to radiation from both
activities, whereas the almost horizontal portion of the
curve is due to P^{32} radiation only. The vertical straight
line is due to S^{35} radiation only.

PLATE I
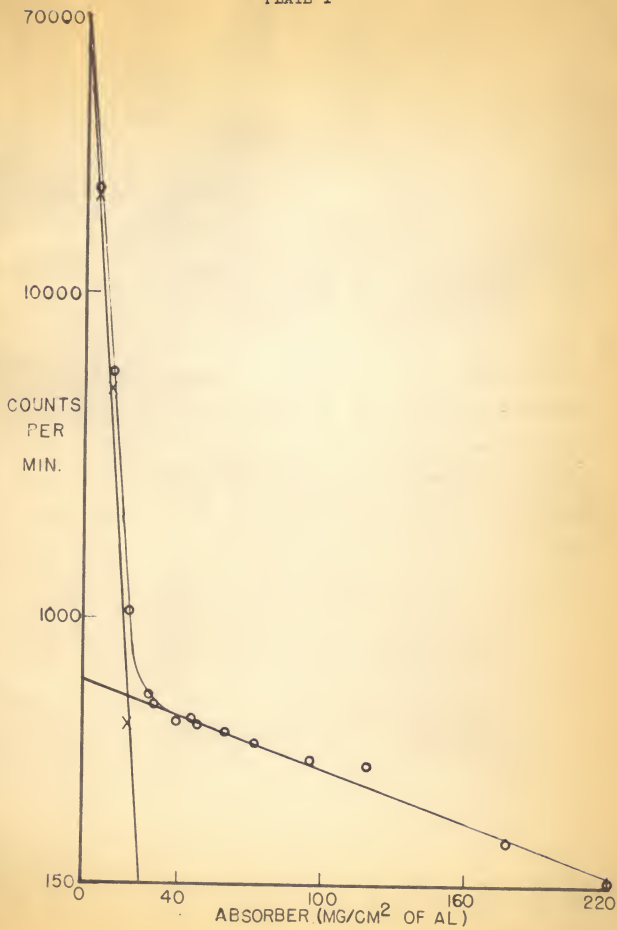
Half-life Determination. An alternate method for the
proof of radioactive purity and the identification of radio-
active elements was half-life data obtained from a sample
of the irradiated PCl_3. The half-lives were obtained from
the plotted results and compared with accepted literature
values. Counting data were taken at zero added absorber
and 34.5 mg./cm.[2] of Al added absorber to distinguish be-
tween S^{35} and P^{32} radiation.

A National Bureau of Standards Ra D-E (β-emitter)
standard was counted along with the sample. This was done
so that all the counting data could be standardized, there-
by eliminating errors due to changing scalers and fluctua-
tions in the G-M tube and scaler circuit. The standard
used was No. 2167 and consisted of 0.876 mg. of Pb elec-
trolytically deposited as PbO_2 on a Ag disc 1/16th inch
thick and faced with a layer of Pd 0.002 inch thick. It
was calibrated by comparison with a standard of the same
isotopes and same physical dimensions which were quanti-
tatively extracted from pitchblende and the disintegration
rate determined from the amount of Ra in the ore. From
this calibration it was computed that the disintegration
rate of this beta ray standard was 216.7 dis/sec. on Aug.
26, 1949. The counting data on the graph had been correct-
ed and standardized prior to plotting.

The half-life values obtained from the graph, Plate II,
for P^{32} and S^{35} are 14.2 days and 87.2 days respectively.
The accepted literature values are 14.3 days (6) and 87.1

EXPLANATION OF PLATE II
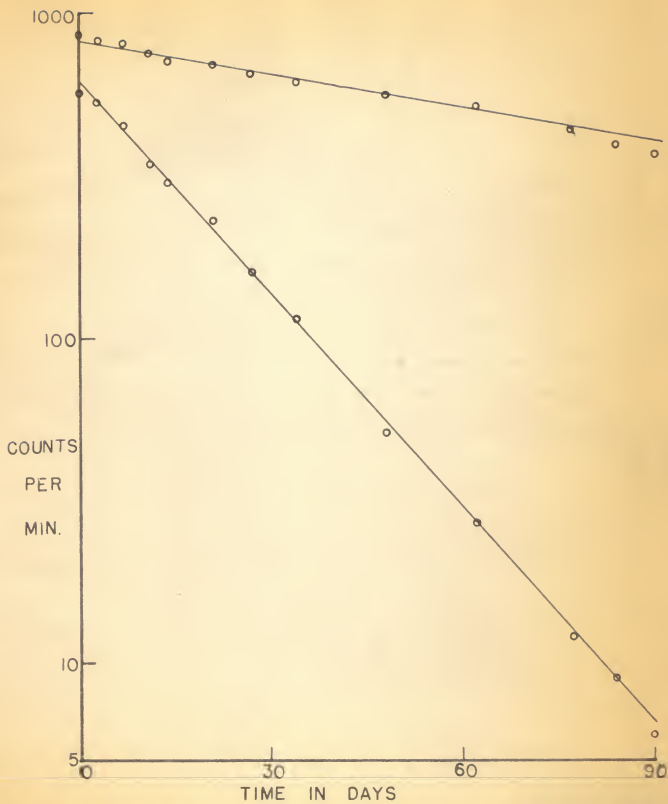
Half-life Curves for P^{32} and S^{35} Radiation
in a Composite Sample

An absorber of 34.5 mg/cm^2 of aluminum was used to
distinguish between the two radiations. The upper curve
is the half-life curve for S^{35}, whereas the lower curve
is the half-life curve for P^{32}.

PLATE II

days (22) respectively. From this favorable comparison
it seemed certain that the only two radioactive elements
produced in the irradiation were P^{32} and S^{35}.

Radiometric Analysis

Elemental inactive sulfur was added to the irradiated
PCl_3, and $PSCl_3$ was synthesized and then distilled. Water
was added to the residue from the distillation and the
water-soluble portion extracted. Barium ions were added
as well as sulfate and sulfite ions as carriers and $BaSO_4$
was precipitated. The precipitate was counted and after
all corrections were applied the counting rate was found
to equal 2952 c/m. Nitric acid was added to the filtrate
oxidizing any other compounds or ions of sulfur to the
sulfate form and barium ions were added again. $BaSO_4$ was
precipitated as before and the precipitate counted. This
counting rate, after corrections equalled 11,412 c/m.

While this was evidence for the existence of sulfate
ion in the bombarded solution, there was a possibility that
hydrolysis of an S^{35} containing compound such as S_2Cl_2 or
SCl_2 could have occurred when H_2O was added. More signifi-
cant perhaps was the greater activity in the second preci-
pitation. This indicated that far more S^{35} was present in
forms such as $S^*_2Cl_2$, S^*Cl_2, $(S^*)=$, $SO_3=$, and PS^*Cl_3 than in
the sulfate form. This agreed with the literature for Koski
(26) had reported that if such compounds as SCl_2, S_2Cl_2 or

$PSCl_3$ existed in the residue, then there should have been considerably more activity in the second precipitate as these compounds were hydrolysed to sulfite ion. Also, according to Koski, more sulfide or free sulfur should have been expected.

The per cent of the total radiation that was due to S^{35} and P^{32} was determined from another three-week irradiation. After the corrections for absorption and dilution were calculated (Appendix II) the percentages were found to be 50% P^{32} and 50% S^{35}.

As was mentioned earlier, S^{35} was incorporated into the parathion molecule during the synthesis of that compound (21). According to the first step of the synthesis (see introduction), the S^{35} had to be present either as elemental sulfur or as already synthesized $PS*Cl_3$. The following experiments were performed to determine this and also to calculate the per cent retention of P^{32} by PCl_3. A one-week bombardment was used for this purpose and the per cent of the total radiation due to P^{32} and S^{35} determined again. These percentages came out to be 42.7% S^{35} and 57.3% P^{32}. Summarizing:

One-week bombardment:-

Total $S^{35} = 7.86 \times 10^9 c/m = 42.7\% = 1.2$ millicuries/gm.of PCl_3

Total $P^{32} = 10.52 \times 10^9 c/m = 57.3\% = 1.6$ millicuries/gm.of PCl_3

Three-week bombardment:-

Total $S^{35} = 1.76 \times 10^{10} c/m = 50\% = 2.4$ millicuries/gm. of PCl_3

Total $P^{32} = 1.755 \times 10^{10} c/m = 50\% = 2.4$ millicuries/gm. of PCl_3

Due to the short half-life of P^{32}, as compared to the time of irradiation, an equilibrium was approached whereby the

rate of formation of P^{32} atoms equaled the rate of disintegration of P^{32} atoms. Therefore, there was relatively little change in the number of P^{32} atoms formed in increasing the time from a one- to a three-week irradiation. S^{35}, however, with a long half-life, as compared to the time of irradiation, was, at three weeks, in a state whereby the rate of formation of S^{35} atoms exceeded the rate of disintegration.

From the irradiated PCl_3, which was 1.9 ml.(3 gms.) in volume, and to which had been added 1.1 ml. of inactive PCl_3, 1.5 ml. of PCl_3 was distilled. From the distillate an aliquot of $10 \mu l$ was withdrawn, and prepared for mounting in the usual way. Twenty-five μl of this prepared solution was mounted on a copper disc and counted. After volume and absorption corrections (Appendix II), the total amount of P^{32} in PCl_3 was obtained. From a knowledge of the total number of inactive phosphorus atoms in the original sample, the per cent retention was calculated, and was found to equal 84.5%.

To the residue from the distillation, which still contained all the S^{35} activity, was added inactive sulfur and $PSCl_3$ was synthesized. Ten μl of the distilled $PSCl_3$ was mounted as previously described and counted. These data gave the total S^{35} activity available in a chemical form that could be incorporated into the $PSCl_3$ molecule. Again the data had to be corrected for absorption and dilution (Appendix II). The final value obtained was 3.96×10^9 c/m.

Since the bombardments were done in closed systems, there was only one factor that could have changed the per cent recombination over the bombardment time interval from one to three weeks. This was the increase in the number of S^{35} atoms formed as the amount of $P*Cl_3$ was constant. This was true since the rate of formation of the S^{35} atoms still exceeded the rate of disintegration at time equal one week, while the rate of formation was almost at equilibrium with the rate of disintegration for P^{32} atoms at the same time. During this time interval, some of the newly formed S^{35} atoms could have reacted with $P*Cl_3$ molecules thereby reducing the number of $P*Cl_3$ molecules. Since this would be a probability function and considering the large excess of inactive PCl_3 molecules compared to the number of active $P*Cl_3$ molecules, it would seem plausible to say that only a very few $P*Cl_3$ molecules would be involved. This would decrease the per cent retention by only a few tenths of a per cent. Therefore the per cent P^{32} activity retained by PCl_3 could be applied directly to a three-week bombardment whereas the amount of S^{35} available for the $PSCl_3$ synthesis could be expanded directly to a three-week bombardment and presumably valid calculations made from these data in conjunction with the rest of the data which were obtained from three-week irradiations.

When the P^{32} activity was counted from the distilled PCl_3 fraction, it was noted that there was some S^{35} activity in the fraction. This was attributed to mechanical

carry over since no holdback carriers were added to the irra-
diated $\left[PCl_3\right]$*,(this symbol refers to the irradiated liquid
in general), and the concentration of the total amount of
compounds containing S^{35} was extremely small.

Experimental Fractionation

A preliminary investigation was undertaken to deter-
mine the degree of separation of the P^{32} and S^{35} activities
by a fractionation procedure. One hundred μl of the bom-
barded solution was added to 3 ml. inactive PCl_3 and 0.3 ml.
$PSCl_3$. Four cuts were taken from this fractionation at temp-
eratures of B_1, 70-76°C; B_2, 76-100°C; C_1, 100-120°C; and C_2,
120-135°C. Two-tenths of a ml. were left behind as a residue .
A sample also had been taken from the original solution and
this was designated as No. 1. Despite the unrefined techni-
que, the data(Table 3) indicated a distribution of activity
that was sufficiently favorable to prompt further investiga-
tion along these lines, using more refined techniques.

Table 3. Preliminary investigation data.

Sample:	Total c/m:	P^{32}c/m:	S^{35}c/m :	% P :	% S
1	3084	1540	1544	49.8	50.2
B_1	1097	1032	59	94.6	5.4
B_2	1451	1096	355	75.5	24.5
C_1	3417	1343	2074	39.3	60.7
C_2	3148	1233	1915	39.2	60.8
Residue	57747	2050	55697	3.5	96.5

A fractional distillation was performed again. One hundred

μl of $\left[PCl_3\right]^*$ were added to 3 ml. of carrier PCl_3 and 3 ml.
$PSCl_3$. Six fractions were taken, aliquots of these fractions
withdrawn, prepared for counting, and counted in the usual
fashion. The data indicated that these six fractions could be
divided into two distinct groupings of P^{32} and S^{35} activity
and so these groups were separated. The second group was
added to the residue from the first distillation along with
an additional ml. of PCl_3 and $PSCl_3$. An additional ml. of
PCl_3 was added also to the first group, and both groups re-
fractionated. The first group contained the first three
cuts of the distillation and the second group contained
the rest.

Five fractions were collected from the redistillation of
the first group and three fractions were collected from the
second, leaving a small residue. Again, counting data were
taken on aliquots prepared in the usual way. The results
from the redistillation indicated good $P^{32} - S^{35}$ activity
separation except in the $PSCl_3$ fraction. This fraction
showed a residual P^{32} activity in all three distillations
that apparently could not be separated. This was indica-
tive of a compound containing both phosphorus and sulfur
and was taken as preliminary evidence for $P*S*Cl_3$ that had
apparently been synthesized during the molecular recombina-
tion characteristic of Szilard-Chalmers type reactions.

Since the per cent retention had already been calculated
and it was known definitely that $P*Cl_3$ was one of the pro-

ducts of the reformation process, it was decided to reduce the specific activity of the $\left[PCl_3\right]^*$ solution by first distilling and discarding the PCl_3. Prior to this, however, 2 ml. of holdback carrier $PSCl_3$ were added. The PCl3 was distilled, and then an additional ml. of PCl_3 was added to the residue and it also was distilled.

The residue left from this distillation contained 2 ml. of $PSCl_3$ and any of the bombarded solution that had not been distilled. This was added to 2.5 ml. PCl_3, an additional ml. $PSCl_3$, 5 ml. S_2Cl_2 and the fractionation performed again. Samples were withdrawn from the three fractions collected (plus the residue), prepared for counting and the $P^{32} - S^{35}$ ratio determined for each fraction. The results indicated poor activity distribution but this was attributed to an inefficient distillation head. Because of this poor distribution each fraction was taken and flooded with its respective principal constituent (inactive form) as follows: 3 ml. PCl_3 were added to the PCl_3 fraction, 2 ml. $PSCl_3$ were added to the $PSCl_3$, and 2 ml. S_2Cl_2 were added to the S_2Cl_2 fraction which was combined with the residue. These flooded samples were fractionated separately with three cuts taken from each one. Aliquots were withdrawn from the middle cut, prepared for counting and counted. The $P^{32} - S^{35}$ ratios between these two distillations indicated that the P^{32} activity was concentrating in the PCl_3 fraction and that the S^{35} activity was concentrating in the S_2Cl_2 fraction. There

was, again, a constant ratio, however, of P^{32}/S^{35} in the $PSCl_3$
fraction. The ratios from these two distillations were 0.0548
and 0.0522 respectively. The new residue also had what appear-
ed to be a constant ratio. The constant ratio in the $PSCl_3$
fraction was interpreted as evidence for a $P*S*Cl_3$ compound
apparently synthesized during reformation of the atoms as
a result of the molecular break-up that occurred due to the
Szilard-Chalmers effect. The constant ratio in the residue
was attributed again to an inefficient separation. The
S^{35} activity in the S_2Cl_2 fraction was indicative of either
the formation of S_2*Cl_2 or elemental S as a result of the
Szilard-Chalmers effect. Since S_2Cl_2 had been added as an
inactive carrier, it would have been impossible to distingu-
ish between the two for it has been known that an exchange
reaction (38) occurred between elemental sulfur and mono-
sulfurchloride (S_2Cl_2) at 100°C. This temperature was
surpassed during the distillations.

To be sure of these constant ratios in the $PSCl_3$ frac-
tion, the middle cuts were flooded again - PCl_3 with 1 ml.
PCl_3, $PSCl_3$ with 1 ml. $PSCl_3$, and S_2Cl_2 (without the residue)
with 1 ml. S_2Cl_2. These data corroborated the data from the
previous distillations, although the P^{32}/S^{35} ratios were
lower in all cases. The ratio for the middle cut of the
$PSCl_3$ fraction was 0.011 but this value must be corrected
for a 10-day decay period before the comparison is made.
From this it was concluded that $P*S*Cl_3$ and $PS*Cl_3$ were

also products of this Szilard-Chalmers type reaction.
Great care was taken throughout to flush and clean the
apparatus between distillations reducing the possibility of
contamination.

Experimental Chromatography

A one-way ascending chromatographic analysis in con-
junction with radioautography was attempted on various
amounts of the irradiated material. This consisted of in-
troducing a sample of material 1 inch from the bottom of a
strip of Whatman #1 filter paper 1 inch wide and 20 inches
long. These strips were suspended from the tops of 1 liter
capacity graduated cylinders in such a manner that approx-
imately $\frac{1}{2}$ the distance between the spot of introduction
and the bottom of the strip was immersed in 50 ml. of eluting
agent. The graduated cylinders were equipped with ground
glass lids so that the strips could be protected from air
currents. The strips were chromatographed to the equilib-
rium position before they were removed from the cylinders
and hung to dry. The sample sizes ranged from 25 to 100 μl.

When the strips were dry, they were placed in contact
with Eastman No-Screen X-ray film and held in position with
"Scotch" tape. The activity was located on the filter paper
strip by comparing the strips to the corresponding blacken-
ing on the X-ray film, the degree of this blackening de-
pending on the amount of activity in any one locality on
the filter strip and the length of exposure.

This method and technique produced no useful data as the phosphorus activity could not be moved from the spot of introduction. The sulfur activity was moved by several eluting agents but no attempt was made to identify the chemical form since the phosphorus activity had not been moved.

After this investigation had been started, published data were found (10) which introduced the idea of pretreating the filter paper before use in chromatography. It was reported that this was the only way the movement of phosphorus compounds could be effected. This paper has already been summarized in the literature survey. One combination was taken from this publication, however, and was chosen from the many reported because it gave the greatest distance of separation of the different chemical entities chromatographed. This combination involved a pretreatment of the filter paper with 8-hydroxyquinoline and the subsequent use of an eluting agent composed of 70% propanol-2, 30% water, and 5% trichloroacetic acid.

Trial runs with this eluting agent using labelled phosphate and elemental sulfur, both obtained from Oak Ridge, evidenced the movement of these two substances. Further, labelled sulfide and phosphite ions were synthesized by the following reactions and these were chromatographed also.

$$2Na + S^* \longrightarrow Na_2S^*$$
$$SO_2 + P^*O_4^= \longrightarrow P^*O_3^= + SO_3 \quad (38)$$

Autographs were made from these four chromatographs and the

R_f values determined from the autographs. The R_f value for phosphate ion compared quite favorably with that reported in the publication which described this eluting agent. This eluting agent was employed for all subsequent chromatographic investigation.

Samples from an irradiated solution of PCl_3 were again chromatographed. Despite the pretreatment, the volatile and reactive sample spread over the lower half of the filter paper during the introduction process and seemed to have reacted with the hydroxyl groups of the filter paper. Also, the eluting agent contained water and so it was quite certain that hydrolysis of some of the sample occurred when the two came into contact.

Although the active sample covered the lower portion of the filter paper, it was chromatographed and autographs made from these chromatographs. Entire areas on the autographs were obscured although a few bands were identifiable. These chromatographs were autographed again 8 weeks later and again 6 weeks after that. This permitted the phosphorus activity to decay almost entirely and permitted the sulfur radiation to blacken the X-ray film. This resulted in the positive identification of elemental sulfur (Plates III, IV, V, and VI). Other bands identified were sulfide, phosphate, and phosphite. However there was considerable doubt whether these last mentioned ions were present in the original sample or formed by the hydrolysis of PCl_3, $PSCl_3$, and S_2Cl_2 by the water in the eluting agent.

PLATE III

A

B

EXPLANATION OF PLATE IV

Original Radioautograph of Chromatographed Sample

A - Sample introduction spot.

B - Area of concentrated radioactive sulfur.

C - Area of unidentifiable phosphorus activity.

PLATE IV

EXPLANATION OF PLATE V

Radioautographs of Chromatographic Strips (Shown
in Plate III) After an Eight-Week Decay Period

A – Sample introduction spot.

B – Area of concentrated radioactive sulfur.

C – Area of unidentifiable phosphorus activity.

PLATE V

A

B

C

EXPLANATION OF PLATE VI

Radioautographs of Chromatographic Strips (Shown
in Plate III) After a Fourteen-Week Decay Period

A - Sample introduction spot.

B - Area of concentrated radioactive sulfur.

C - Area where unidentifiable phosphorus activity
had been.

PLATE VI

Column Extraction

Since satisfactory results could not be obtained through the use of paper chromatography, an inert column extraction using a non-polar eluting agent was attempted. For this purpose a column 13 inches long and 0.50 inch inside diameter was built using an alumina bed. Benzene was used as the eluting agent.

In a preliminary run, 100 μl PCl_3 were adsorbed on the alumina bed. With a slight gravity head, a flow rate of 2.5 ml./min. for the eluting agent was maintained. The method chosen for detecting PCl_3 or hydrolysis products in the eluate was based on the silver chloride test. No chloride ion was found in 1500 c.c. of benzene collected from the column but it was noted that a robin's egg blue band formed when the PCl_3 came into contact with the alumina. With further eluting, this band faded into two yellow bands and a broad gray band. Upon the supposition that this column was too long, for the time involved and the volume of eluting agent required, a shorter column was built.

This column was 3.5 inches long and 0.48 inch inside diameter and alumina was used again for the adsorbing material. Chloride ion was eluted through this one too quickly and so the height of the bed was extended to 5 inches. A 100 μl sample of PCl_3 was eluted through this column with 400 c.c. of benzene at a flow rate of 2.5 ml./min. No colored bands were noted at all.

One hundred μl of $\left[PCl_3\right]^*$ was introduced at the top of the column but beneath the surface of the benzene and a radioactive column extraction was attempted using the 5-inch column. A liter of benzene followed by a liter of chloroform failed to elute any P^{32} activity through the column and no chloride ion was found upon the addition of $AgNO_3$ to the organic solvents. The first 400 c.c. of benzene were collected in ten ml. fractions. Every fifth sample, together with samples from the remaining benzene and the chloroform (both collected in batch quantities), were prepared for counting in the usual manner. The samples were counted for S^{35} activity, the principal quantity of the activity having been eluted into the chloroform fraction, although most of the samples had S^{35} activity present. No attempt was made to interpret these data.

Another column 13 inches long and 0.48 inch inside diameter was constructed. A magnesia bed was used in this column after the magnesia had been dried at 750°C for 4 hours. One hundred μl of $P*Cl_3$ was introduced at the top of the column and beneath the surface of benzene. The flow rate on this siphon pressure column was 1 c.c./3 min. Since the activity could not be moved utilizing 600 c.c. of benzene, the idea was abandoned.

One last experiment was attempted using a more polar solvent. Six hundred c.c. of acetone were eluted through the column and a very small fraction of P^{32} activity was de-

tected in the collected solution. However, there were in-
dications that the remaining amount of $P*Cl_3$ was definitely
affixed to the magnesia within the column.

DISCUSSION

Limitation of Study

There was, of course, a natural limitation in the de-
gree of accuracy of a study of this type. This limitation
was due to the randomness of counting events. This was min-
imized, but not completely eliminated by taking a great num-
ber of counts or by counting over a longer period of time.
Both of these methods helped reduce experimental error.
In addition to this inherent error in the counting data,
it was felt that an error was introduced by using a frac-
tionation column of unknown efficiency. Certainly this
error was not very large as evidenced by the small amount
of any apparent radioactive contamination. However, work-
ing with small quantities as in this study, caused forced
heating conditions in some cases and super heating could
have occurred.

A reagent grade of PCl_3 was ordered and supplied by
Oak Ridge as the starting material. As the preparation for
bombardment was handled by them there is an element of uncer-
tainty as to the final chemical purity of the sample immed-
iately prior to the irradiation. However, any error intro-
duced in this way should be small. There is also no know-
ledge concerning reactions due to beta radiations that could
have taken place after the bombardment ceased.

Further, this study was somewhat limited by the extreme

reactivity of PCl_3 and the ease of hydrolysis of PCl_3, $PSCl_3$, and S_2Cl_2. Although every effort was taken to keep experimental conditions as anhydrous as possible, there were still times when contact between the sample and the atmosphere were unavoidable.

Preferential Reaction and Kinetics

Experimental. The total number of atoms of $P*S*Cl_3$ and $PS*Cl_3$ synthesized in the bombardment could be calculated from corrected data obtained from the fractionation procedures (Appendix III), and the number of S^{35} atoms in a suitable form for induction into the PCl_3 molecule could be calculated from corrected data obtained from the thiophosphoryl chloride synthesis. The difference between these two values should have been the number of atoms of elemental sulfur formed in the bombardment. These values were 1.97×10^{14} atoms of $S*$ either as $P*S*Cl_3$ or $PS*Cl_3$ and 16×10^{14} atoms of sulfur in a suitable form for induction into the PCl_3 molecule. The difference was 14×10^{14} atoms of elemental sulfur synthesized in the bombardment.

The number of active sulfur atoms in $PS*Cl_3$ could be calculated from the corrected data obtained from the fractionation procedures. The number of P^{32} atoms in the $PSCl_3$ fraction were calculated first. Since every P^{32} must have an S^{35} with it the only sulfur present was radioactive sulfur, and the number of P^{32} atoms equaled the number of S^{35}

atoms in the $P*S*Cl_3$ molecules. The value found in this fashion was 3.51×10^{12} atoms of sulfur. Now, by subtracting this value from the total number of S^{35} atoms in the $PSCl_3$ fraction, the number of $PS*Cl_3$ molecules was obtained. This value was 1.93×10^{14} molecules of $PS*Cl_3$ (Appendix III).

The number of $P*Cl_3$ molecules was obtained from the total amount of P^{32} activity and the per cent recombination of the P^{32} into the mother molecule. This value was 4.4×10^{14} atoms (Appendix III). Then, since the bombarded sample was 3 gms. in weight, the number of inactive PCl_3 molecules prior to the irradiation could be calculated. This was found to be 1.305×10^{22} molecules.

From these calculated values, the following ratios were determined:

$$\frac{PCl_3}{P*Cl_3} = \frac{1.305 \times 10^{22}}{4.4 \times 10^{14}} = 2.97 \times 10^7$$

$$\frac{PS*Cl_3}{P*S*Cl_3} = \frac{1.935 \times 10^{14}}{3.51 \times 10^{12}} = 55$$

From the large excess of inactive PCl_3 atoms and from an apparent equal probability of the formation of $PS*Cl_3$ and $P*S*Cl_3$ molecules, it was expected that the $PS*Cl_3$ / $P*S*Cl_3$ ratio would have been of the order of magnitude of the $PCl_3/P*Cl_3$ ratio. This was not the case, however, as evidenced by the ratio of $PS*Cl_3$ to $P*S*Cl_3$. It was concluded therefore that a preferential reaction between the molecule $P*Cl_3$ and the atom $S*$ existed, both reactants

having been in activated states. The greater portion of
the total amount of P*S*Cl$_3$ formed would have resulted from
a mechanism that involved the regeneration of the mother
molecule first, and then the subsequent reaction with the
labelled sulfur. If this were true, it would seem that the
formation of P*S*Cl$_3$ would depend upon the length of life
of the newly formed, unreacted, labelled sulfur. The labelled
sulfur did have a length of life sufficient to permit this
reaction. This was verified by the fact that over half of
the sulfur activity in the bombarded liquid was in the form
of elemental sulfur. This indicated the number of cooling
collisions that could have been suffered by the sulfur with-
out having been involved in a reaction.

In this extremely high energy system, free radicals
were omnipresent. Also, it was expected that the γ-ray
emitted by the compound P^{32} nucleus and the proton emitted
by the compound Cl^{36} nucleus would have caused the shear-
ing of electrons from these atoms. The effects due to
these two phenomena could have been the formation of many
unusual molecules. Because of the omnipresent free radicals,
another mechanism was postulated. This mechanism could
account for the formation of P*Cl$_3$, P*S*Cl$_3$ and PS*Cl$_3$.

$$1) \quad P* + Cl \longrightarrow P*Cl$$
$$2) \quad P*Cl + Cl \longrightarrow P*Cl_2$$
$$3) \quad P*Cl_2 + S* \longrightarrow P*S*Cl_2$$
$$4) \quad P*S*Cl_2 + Cl \longrightarrow P*S*Cl_3$$

Any one of these reactions could have been the initiating step depending upon the fragments that resulted from the molecular break-up. Also, reaction No. 3 could have occurred any place in the series.

From the theoretical applications that follow, it was believed that the principal mechanism for the formation of $P*Cl_3$ was direct collision between a P^{31} atom and a P^{32} atom. The P^{32} atom was stopped in the vicinity of the three chloride ions or atoms while the P^{31} atom was driven from the reaction cage surrounding the vicinity of the collision. Viz.

$$P^{32} + P^{31}Cl_3 \longrightarrow P^{32} + 3Cl \longrightarrow P^{32}Cl_3$$
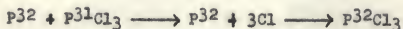
Theoretical. The theory, previously advanced by Libby et al. (14, 17, 30) for the phenomenon of hot atom chemistry as related to organic compounds, (reviewed in the Literature Survey), considers the possible reactions as falling into two classes that correspond to the energy of the recoiling radioactive atom. Reactions that occurred in the high energy range (in relation to the energy of a chemical bond) were called "hot" and those that occurred in the range where the energy was still somewhat larger than the chemical bond but not over two- or threefold larger, were called "epithermal". Further, the reactions that lead to the retention of the radioactive atom in the mother molecule take place in the hot range, while the epithermal reactions are supposed to devolve around solvent cage action

and account for the formation of new molecules.

Applying this theory to the work and results described in this paper, it is seen that the formation of P*Cl$_3$ occurred principally in the hot range. The momentum of the hot P* atom could have been completely transferred or lost through collision with Cl, S^{35}, or another inactive P atom. This would have left any molecular fragments formed and the stopped P* atom in the same solvent cage, making possible the reformation of the mother molecule or in slight amounts the synthesis of P*S*Cl$_3$ or PS*Cl$_3$. This explanation would account also for the higher percentage retention obtained in this work, than obtained by Libby et al. in their work on organic halides, because the inactive halide atom in the organic halide molecule was the only atom that could have stopped the hot halide atom. On the other hand, every atom in PCl$_3$ could have stopped the recoiling hot atoms, and so virtually every head-on collision of an active atom in the hot energy range could have resulted in a complete trans-fer of momentum leaving the free radicals and the hot atom in the same solvent cage.

The formation of P*S*Cl$_3$, PS*Cl$_3$, and elemental sul-fur would have occurred in the epithermal energy range. This would have been due to glancing collisions between the recoiling hot atom and other atoms or molecules present, causing a transfer of the momentum of the recoiling atom step by step until it eventually was in the epithermal

range and in a reaction cage in which free radicals did not
exist. From there it could "cool" further or react with
PCl_3 or $P*Cl_3$ giving $PS*Cl_3$ or $P*S*Cl_3$. The theory proposed
by Libby and co-workers, then, would seem to fit this system,
as well.

In the closed system in which the PCl_3 was irradiated,
it did not seem likely that the ions phosphite, phosphate,
sulfite, and sulfate could have been formed. Chromatogra-
phic evidence was obtained for these ions but it must be
remembered that the eluting agent contained water and these
ions are formed by hydrolysis of S_2Cl_2, PCl_3, and $PSCl_3$.
It seems doubtful that these ions were formed as a result
of the bombardment. Chromatographic evidence was also ob-
tained for the sulfide ion and, of course, this was a possible
product of the bombardment. No other evidence was obtained,
however, and therefore its existence must remain questionable.

SUMMARY

Radioactive phosphorus and sulfur were shown to have been the only activities produced in the slow neutron irradiation of PCl_3. The specific activity of both of these activities was found to increase to a limit as the bombardment time was increased. The per cent of P^{32} retained or captured reforming the mother molecule, PCl_3, was calculated and equalled 84.5%. Evidence for the formation of thiophosphoryl chloride, $P^{32}S^{35}Cl_3$ and $PS^{35}Cl_3$, was presented as well as the ratio of $PS^{35}Cl_3$ atoms/$P^{32}S^{35}Cl_3$ atoms calculated. This equalled 55. The ratio of PCl_3 atoms/$P^{32}Cl_3$ atoms formed equalled 2.97×10^7.

Proof was extended for the formation of elemental S^{35} and labelled monosulfur chloride (S_2Cl_2), both formed as a result of slow neutron capture.

From the ratios calculated, a preferential reaction was postulated along with possible mechanisms for the formation of these active products. Further, it was found that the production of these active compounds could be accounted for by an existing theory, and a reason was given to explain why no oxygen containing compounds could have been expected from the bombardment. Evidence for these oxygen compounds as well as for sulfide ion was obtained but it was not considered substantial.

ACKNOWLEDGEMENTS

APPENDICES

Appendix I

In the following calculations an 8% correction factor is used for counting geometry. In other words, about 8% of the disintegrations that take place are actually being counted. This low percentage count is due to the relation of the stage on which the sample was placed to the G - M tube. Such a correction is necessary since the sample emits radiations in all directions.

To illustrate the validity of this 8% factor, a Standard Ra D-E beta emitter was counted at zero added absorber and under the same geometry conditions from which the counting data were obtained. From an absorption curve supplied with the standard by the National Bureau of Standards, it was determined that a ratio of 1.11 existed between the counting rate with no added absorber and the true zero absorber. Application of this correction alters the counting rate obtained as follows:

$$800 \text{ c/m} \times 1.11 = 890 \text{ c/m}$$

The disintegration rate for the standard was given as $216.7 \text{ dis}/_{sec} \times 60 \text{ sec}/_{min.} = 1.3 \times 10^4 \text{ dis}/\text{min.}$ The sample was calibrated 3 years and 3 months ago, so applying half-life corrections based on the half-life of Ra D taken as 22.2 years, (see next page)

$$A = A_0 \, e^{-\lambda t}$$

where A_0 = initial activity

A = final activity

λ = decay constant.

$$= \frac{.693}{t_{\frac{1}{2}}} = \frac{.693}{22.2 \text{ yrs}}$$

$$A = A_0 e^{-\frac{.693}{22.2 yr} \times 3.33 yr} = 1.3 \times 10^4 \text{ dis}/m \cdot e^{-0.103}$$

$$e^{-0.103} = .90$$

$$A = 1.3 \times 10^4 \text{ dis}/m \times .9 = 1.17 \times 10^4 \text{ dis}/min.$$

This same sample was counting only 890 c/m. This was $\frac{890}{1.17 \times 10^4} \times 100$ which equalled 7.6% of the total activity.

Appendix II

Example of Correction Calculations

The example selected is the correction for total S^{35} and P^{32} activity in the distilled $PSCl_3$ fraction.

S^{35} activity = 2014 c/m.

Correction for air and window thickness is a factor of 3 obtained by graphic extrapolation (Plate I)

2014 c/m $\times$ 3 = 6042 c/m.

Geometry correction = $\frac{6042}{.08} = 7.55 \times 10^4$ c/m.

Half-life correction:

$$\frac{A}{A_0} = e^{-\lambda t} = e^{-\frac{.693}{87.2d} \times 46d} = e^{-0.365} = 0.69$$

$$A_0 = \frac{A}{0.69} = \frac{7.55 \times 10^4 c/m}{0.69} = 1.09 \times 10^5 c/m$$

Volume corrections: The volume of the S^{35} activity

formed in the irradiated solution was assumed to be
negligible. This seemed reasonable after considering
the total number of atoms and the number of S^{35} atoms
that were formed. The irradiated solution was assumed
to be pure PCl_3. The sample was diluted with 5 ml. of
inactive $PSCl_3$ and a 1 ml. $PSCl_3$ fraction distilled.
One hundred μl from the distilled fraction was oxi-
dized and diluted to 10 ml. A 50 μl sample was with-
drawn from the diluted sample for counting. Working
backwards:

1.09 x 10^5 c/m for 50 μl x 2 = 2.18 x 10^5 c/m for 0.1 ml.
2.18 x 10^5 c/m for 0.1 ml. x 100 = 2.18 x 10^7 c/m for 10 ml. =
2.18 x 10^5 c/m for 0.1 ml. x 10 = 2.18 x 10^8 c/m for 1 ml.
2.18 x 10^8 c/m for 1 ml. x 5 = 1.09 x 10^9 c/m for 5 ml. or
total sulfur activity in $PSCl_3$.

P^{32} activity = 104 c/m. Here the beta ray is sufficiently
energetic that the correction for air and window thick-
ness is negligible (proven by graphic extrapolation in
Plate I).

Geometry correction = $\frac{104}{.08}$ = 1.3 x 10^3 c/m.

Half-life correction:

$$\frac{A}{A_o} = e^{-\lambda t} = e^{-\frac{.693}{14.3\ d/y} \times 46\ d/y} = e^{-2.23} = 0.11$$

$$A_o = \frac{A}{0.11} = \frac{1.3 \times 10^3 c/m}{0.11} = 1.18 \times 10^4\ c/m$$

Volume corrections: these are the same as for S^{35}, in
this case. Final activity = 1.180 x 10^8 c/m for 5 ml. or

total P^{32} activity.

Appendix III

The Calculation of the Number of Active Atoms on a
Specific Day (Day of Receipt of Sample) from a Known
Activity.

No. of atoms = $\frac{A}{\lambda}$ where A = activity

λ = decay constant

Example: Number of active atoms of PCl_3.

Total P^{32} activity x % retention = activity due to P^*Cl_3.

1.755×10^{10} c/m x $0.845 = 1.48 \times 10^{10}$ c/m

$$N^{P32} = \frac{1.48 \times 10^{10} c/m \times 60 \text{m}/hr \times hr/day}{\frac{0.693}{14.3 \text{ days}}}$$

$$= \frac{1.48 \times 10^{10} \times 60 \ 24 \ c/day \times 14.3 \text{ days}}{0.693}$$

$$= 4.4 \times 10^{14} \text{ atoms of } P^*Cl_3$$

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A STUDY OF THE CHEMICAL EFFECTS OF SLOW NEUTRON
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by

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Since the chemical species produced by neutron irradiation are dependent upon the bond energies and the systems being irradiated, the effects are varied from compound to compound and system to system. A study of these effects was desirable so that the results could be predicted for related compounds. Further, this research was undertaken on a compound not previously studied, phosphorus trichloride, to contribute more information concerning the fundamental nature of the Szilard-Chalmers type reaction and to examine the theoretical applications in light of a new system.

It was shown mathematically that the recoil energy of an atom after emitting one or more stabilizing gamma rays was sufficient to break a chemical bond. In this particular research it was noted that both active phosphorus (P^{32}) and active sulfur (S^{35}) was formed as a result of the slow neutron bombardment of phosphorus trichloride. Also, it was shown that no chlorine activity was present.

The specific activity of both P^{32} and S^{35} present was found to increase to a limit as the bombardment time was increased. The per cent of P^{32} retained or captured reforming the mother molecule, PCl_3, was calculated and equalled 84.5%. Evidence for the formation of thiophosphoryl chloride, $P^{32}S^{35}Cl_3$ and $PS^{35}Cl_3$, was presented as well as the ratio of $PS^{35}Cl_3/P^{32}S^{35}Cl_3$ atoms calculated. This equalled 55. The ratio of $PCl_3/P^{32}Cl_3$ atoms formed equalled 2.97×10^7.

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